peak at m/e 437 for $C_{25}H_{27}O_6N$. The nmr spectrum in $CDCl_3$ showed NCH_3 (3 H singlet, δ 2.10), acetoxy protons (6 H singlet, δ 2.28), CH_2CH_2 (4 H multiplet, δ 2.9), 8-methylene (2 H broad singlets, δ 3.11 and 3.34), two OCH_3 (6 H singlets, δ 3.62 and 3.80), two vinylic protons (2 H singlets, δ 4.97 and 5.63), and four aromatic protons (4 H, δ 6.24, 6.50, 7.02, and 7.29).

The exocyclic double bond in diacetate XII was readily reduced with Adams catalyst. The resulting oily dihydrodiacetate, M^+ m/e 439 for $C_{25}H_{29}O_6N$, exhibited an nmr spectrum whose most salient feature was a C-13 methyl doublet, centered at δ 0.95, $J = 6.5$ Hz.

The rearranged product XII must have been formed from the methobromide IX through intermediates X and XI, *i.e.*, by a route that may very well parallel the biogenetic sequence for ochotensimine (II).[6,7]

Acknowledgments. The authors are grateful to Professor J. E. Baldwin for useful discussions, to the National Institutes of Health for research fellowship 2 F01 GM-33,013-03 to C. D. J., and for research grant GP-9359 from the National Science Foundation.

[6] Two syntheses of ochotensimine by classical routes have been reported; see (a) S. McLean, M.-S. Lin, and J. Whelan, *Tetrahedron Letters*, 2425 (1968); (b) T. Kametani, S. Takano, and S. Hibino, *J. Pharm. Soc. Japan*, **88**, 1123 (1968); (c) H. Irie, T. Kishimoto, and S. Uyeo, *J. Chem. Soc., C*, 3051 (1968).

[7] Satisfactory elemental analyses were obtained for all key intermediates.

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Received April 7, 1969

Deuterium Tracer Studies of Tricarbahexaborane(7) Formation. Synthesis of the 2,4-$(CH_3)_2C_3B_3H_4^-$ Ion and 2,4-$(CH_3)_2$-μ-D-$C_3B_3H_4$

Sir:

The characterization of a C-methyl derivative and two C,C′-dimethyl derivatives of the open-cage carborane $C_3B_3H_7$ (*nido*-2,3,4-tricarbahexaborane(7)) as the principal volatile products in the vapor-phase reaction of tetraborane(10) with acetylene at 25–50° has been reported.[1-3] We now present some additional findings on the formation and chemistry of this carborane cage system. The vapor-phase reaction of C_2D_2 with an equimolar amount of B_4H_{10} at 50° in a sealed Pyrex bulb yields three major volatile products whose infrared and mass spectra[2] and glpc retention times clearly identify them as deuterated tricarbahexaborane(7) derivatives corresponding to those obtained from the C_2H_2–B_4H_{10} reaction, *e.g.*, 2-methyl-, 2,3-dimethyl-, and 2,4-dimethyl-2,3,4-tricarbahexaborane(7). Significantly, all deuterium incorporated into these products appears to be bound to carbon; no evidence for either terminal or bridge B–D bonds can be detected in the infrared spectra of the carboranes or in those of the B_2H_6 and B_4H_{10} recovered from the reaction. Cage C–H bands (~3020 cm^{-1}), which are present in the ir spectra of isotopically normal $C_3B_3H_7$ derivatives,[2] are absent in the products of this study, and the methyl C–H band (normally a multiplet) is a single strong absorption at 2940 cm^{-1} in all three spectra. Medium absorptions at 2270 and 2170 cm^{-1} in each spectrum (not present in the nondeuterated compounds) are attributed to cage C–D and methyl C–D stretch, respectively.

The mass spectra of all three tricarbahexaborane products exhibit sharp cutoffs corresponding to the tetradeuterated species, *e.g.*, at m/e 94 for the monomethyl derivative ($^{12}C_4{}^{11}B_3{}^1H_5{}^2D_4{}^+$) and at m/e 108 for each of the dimethyl derivatives ($^{12}C_5{}^{11}B_3{}^1H_7{}^2D_4{}^+$). The presence of trideuterated species is also indicated, however, by comparison of the fragmentation patterns with those of the isotopically normal compounds. When the C_2D_2–B_4H_{10} reaction is carried out with a 10:1 excess of C_2D_2, the relative abundance of tetradeuterated *vs.* trideuterated species in each spectrum increases approximately fourfold compared to the 1:1 reaction, as estimated from the cutoff peak intensities.

The possibility that some incorporation of deuterium into the carborane products may occur *via* direct exchange of the latter with C_2D_2 has been examined by exposing 2-$CH_3C_3B_3H_6$, 2,3-$(CH_3)_2C_3B_3H_5$, and 2,4-$(CH_3)_2C_3B_3H_5$ to a 100-fold excess of C_2D_2 at 50°. After 10 days mass spectroscopic analysis of all compounds involved gave no evidence of deuterium exchange.

These data point to a minimum of C–D bond breaking during formation of the tricarbahexaborane derivatives, and in this respect parallel the synthesis[4] of C_2D_2–B_4H_6 (2,3-dicarbahexaborane(8)-d_2) from C_2D_2 and B_5H_9. However, while the formation of the dicarbahexaborane requires no C–C breakage, such cleavage is clearly involved[3] in the preparation of both $(CH_3)_2C_3B_3H_5$ derivatives from C_2H_2. Rate studies of this reaction are now in progress and may provide additional clues to the reaction mechanism.

The reaction of either isotopically normal C,C′-dimethyl derivative with excess sodium hydride in dry diglyme or tetrahydrofuran (THF) proceeds smoothly at room temperature, producing a volume of H_2 consistent with the reaction

$$(CH_3)_2C_3B_3H_5 + H^- \longrightarrow (CH_3)_2C_3B_3H_4^- + H_2$$

Typically, 0.930 mmole of the carborane reacted with 1.17 mmoles of NaH suspended in mineral oil to yield 0.923 mmole of H_2 (collected in a Toepler pump). The ions apparently produced (2,3- and 2,4-dimethyl-2,3,4-tricarbahexaborate(−1)) are readily hydrolyzed on exposure to moist air and slowly decompose even in dry diglyme solution. It is clear that the $(CH_3)_2C_3B_3H_4^-$ ions are formed by removal of a bridge proton from the neutral carborane, since treatment of a THF solution of sodium 2,4-dimethyltricarbahexaborate(−1) with excess deuterium chloride produces 2,4-dimethyl-μ-deuteriotricarbahexaborane(7).

$$Na^+(CH_3)_2C_3B_3H_4^- + DCl \longrightarrow NaCl + (CH_3)_2C_3B_3H_4D$$

The infrared spectrum of the carborane product is very close to that of 2,4-$(CH_3)_2C_3B_3H_5$[2] except for the virtual absence of the B–H–B stretch at 1950 cm^{-1} and the appearance of a medium band at 1550 cm^{-1} which is assigned to B–D–B absorption. No terminal B–D or C–D bands are observed. The mass spectrum has a sharp cutoff at m/e 105, corresponding to the $^{12}C_5{}^{11}B_3$-

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[4] J. R. Spielman, R. Warren, G. B. Dunks, J. E. Scott, Jr., and T. Onak, *ibid.*, **7**, 216 (1968).

${}^1H_{10}{}^2D^+$ ion. The 32.1-MHz ${}^{11}B$ nmr spectrum (THF solution) contains two doublets (δ +52.8 ppm relative to $BF_3O(C_2H_5)_2$, J = 180 cps, area 1; δ +2.5, J = 157 cps, area 2), assigned to the coupling of terminal hydrogen atoms with apex and base borons, respectively. The low-field doublet shows no secondary splitting,[1] confirming that the molecule is bridge deuterated. For comparison, the ${}^{11}B$ nmr spectrum of isotopically normal 2,4-$(CH_3)_2C_3B_3H_5$ in THF contains doublets of area 1 (δ +51.6 ppm, J = 178 cps) and area 2 (δ +2.5 ppm, J = 157 cps), with each peak of the low-field doublet further split (J = 49 cps) due to coupling of the two basal boron atoms with the bridge proton.[1]

The tricarbahexaborate(1−) ion presumably contains a basal C_3B_2 ring having three delocalized electron pairs, as does $C_5H_5^-$, and therefore in principle should be capable of π bonding to transition metal atoms to form analogs of the metallocenes and the dicarbollyl complexes. However, reactions of the sodium salts of 2,3- and 2,4-$(CH_3)_2C_3B_3H_4^-$ with anhydrous $FeCl_2$ and $Mn_2(CO)_{10}$ are complex, involving partial decomposition of the carborane ions. Studies of reactions of this type are proceeding and will be reported subsequently.

Acknowledgments. This work was supported by the Office of Naval Research. We thank R. Bishop and T. P. Pitner of this department for obtaining the 32-MHz boron nmr spectra.

(5) National Science Foundation Predoctoral Fellow.

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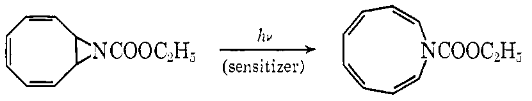
Received April 14, 1969

N-Carbethoxyl-1-azacyclonona-2,4,6,8-tetraene

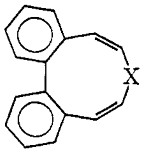
Sir:

We have, for some time, been interested[1,2] in azacyclonona-2,4,6,8-tetraene as it represents a "4n + 2" (n = 2) π-electron homolog of pyrrole.

Hückel theory clearly predicts π-electron stability for this substance[1] while analogy with the already known[3-5] iso-π-electronic, nine-membered monocycle, cyclononatetraenide suggests that perhaps in the all-*cis* arrangement π-electron stabilization of the compound may more than compensate for the obvious energetic disadvantage due to angle strain. For these reasons, interest in the synthesis of 10π-electron heteromonocycles has been quite extensive in recent years. To date, however, pertinent reports deal solely with the synthesis of dibenzoxonin (**2a**) and dibenzothionin (**2b**)[6] and the postulated intermediacy of oxonin upon photolysis of the epoxide of cyclooctatetraene.[7] Presently we briefly describe the synthesis of **1**, the *first* parent 10π-electron heteromonocycle, and for that matter the first isolable uncharged 10π monocycle.



3 **1**



2a, X = O
b, X = S

1 was synthesized along the lines first suggested by us[2] on the basis of orbital symmetry.[1] Thus, brief (1 hr) through-Pyrex illumination of a cold (0°) ether solution of **3** in the presence of benzophenone, with a Hanovia light source produces a mixture, the nmr spectrum of which displays, besides absorption due to benzophenone and **3**, an AB quartet with doublet components centered at τ 3.6 (2 H) and 4.7 (2 H) (J = 10 cps) and a fairly narrow multiplet at 4.2 (4 H).[8] The position and relative areas of these signals are uniquely consistent with a fully unsaturated monocycle. Furthermore, the product, though moderately stable at 0°, is thermally unstable at room temperature, undergoing valence tautomerism to what appears to be N-carbethoxy-8,9-dihydroindole. The thermolysis of **1** is conveniently monitored by nmr at room temperature, the aforementioned signals disappearing with the concurrent appearance of absorptions expected of a dihydroindole structure.

Secure chemical evidence for structure **1** derives from the following experiments. Treatment of the crude photolysis mixture ([**1**]/[**3**] ~ 1) with diimide at either 0 or −78°[9] produced a mixture of partially hydrogenated products. This was subsequently subjected to catalytic (Rh–C) hydrogenation at atmospheric pressure and room temperature to produce fully hydrogenated (nmr) components. Perhydro-**1**,(**4**), was identified both by its nmr spectrum in the mixture and the ir of a pure sample collected gas chromatographically. In both cases identification rests on direct spectral comparison with authentic **4** prepared from azacyclononane and ethyl chloroformate. In either run however it was noticed that the ratio of **4** to hydrogenated **3** was slightly larger than that of their respective dehydro precursors **1** and **3**. This piece of information suggested that perhaps **3** does produce a small amount of **4** under the reductive treatment. A control experiment employing **3** and benzophenone but no **1** demonstrated that this is indeed the case, the proportion of **4** to hydrogenated **3** in the product mixture being determined at *ca.* 1:9. Entirely definitive structural proof for **1** derives from direct low-temperature (0°), catalytic (Rh–C) hydrogenation of the photolysis mixture ([**1**]/[**3**] ~ 1) to produce a 1:1 mixture (nmr, gc) of **4** and hydrogenated **3**. Significantly, catalytic hydrogenation of a mixture of **3** and benzophenone under identical conditions produced no detectable amount (<4%) of **4**.

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(8) Note that the nmr spectrum of the photoproduct is entirely anallogous to that of **2a** which displays, besides aromatic absorption, an AB quartet with doublet components centered at τ 3.95 (2 H) and 4.70 (2 H).[6]

(9) Generated essentially by the procedure described by E. E. Van Tamelen and T. L. Burkoth *J. Am. Chem. Soc.*, **89**, 151 (1967).